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Activity coefficient and excess Gibbs free energies of allyl alcohol with trichloroethylene[1]

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Abstract

Isobaric vapour–liquid equilibrium data have been measured for allyl alcohol and trichlorethylene at 200, 500 and 705 Torr for ten compositions spread evenly over the entire liquid mole fraction range, employing a Swietoslawski-type ebulliometer. The mole fraction composition vs. boiling point data are well represented by the Wilson model. The optimum Wilson parameters are used to calculate the vapour compositions, activity coefficients and the excess Gibbs free energy.

Keywords: Activity coefficient; Allyl alcohol; Trichloroethylene

1. Introduction

In continuation of our interest in the phase equilibria of binary mixtures with an alcohol as one component and a chloro-hydrocarbon as the other [1–3], this study on the vapour–liquid equilibrium of allyl alcohol (1) + trichloroethylene (2) mixtures is reported. There is no published information on the phase equilibrium of this system. The composition (x)–bubble temperature (T) relations have been measured at 200, 500 and 705 Torr to study the effect of pressure on the phase equilibrium.

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2. Experimental

A Swietoslawski–type ebulliometer, very similar to the one described by Hala et al. [4], was used. Connection of the ebulliometer to a good vacuum system, through an in-line mercury manometer facilitated the creation and maintenance of the chosen pressure within ± 1 Torr. The equilibrium temperatures were measured to an accuracy of ±0.1°C by means of a carefully calibrated mercury-in-glass thermometer. The mixtures were prepared gravimetrically and placed in the ebulliometer. The heating rate was adjusted to yield the desired condensate drop-rate of about 30 per minute, as suggested by Hala et al. [4]. The equilibrium temperature was measured after maintaining the steady drop-rate for a sufficient length of time (at least 30 min) and the thermometer showed no change in temperature for at least 15 min.

3. Materials

Allylalcohol (2-propen-1-ol) (Ar grade, SD Fine-Chem. Ltd, Boisar (India)) was distilled twice and the middle fraction of the second distillation was collected for use in the experiments.

Spectroscopic grade trichloroethylene (SD Fine-Chem. Ltd., Boisar (India)), was steam-distilled from 10% calcium hydroxide slurry. The organic phase was collected at − 30 to − 50°C and ice removed by filtration. The filtrate was fractionally distilled twice. The middle fraction of the second distillation was stored in amber-coloured bottles for use in the experiments.

A packed column of length equal to 30 theoretical plates was employed for the purification of both substances. Based on the comparison of the physical properties with literature values [5, 6] presented in Table 1, the substances were expected to be at least 99.8% pure.

4. Results and discussion

Experimental mol fraction –boiling point (x–T) measurements are correlated using the Wilson equation in the form

$$\ln \gamma_1 = -\ln[x_1 + \Lambda_{12}x_2] + x_2\left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{x_2 + \Lambda_{21}x_1}\right] \tag{1}$$

Table 1
Comparison of physical properties of pure liquids at 298.15 K with literature data

Substance	Density (g cm^{-3})	Refractive index	Ref.
Allyl alcohol	0.8523	1.4312	This work
	0.8520	1.4310	[5]
Trichloroethylene	1.4639	1.4781	This work
	1.4640	1.4782	[6]

Table 2
Antoine constants of the pure liquids used in this work

Substance	A	B	C
Allyl alcohol	7.34110	1271.47	188.00
Trichloroethylene	7.02808	1315.04	230.00

Table 3
Vapour–liquid equilibrium of the allyl alcohol (1) + trichloroethylene (2) system: Wilson parameters: $(\lambda_{12} - \lambda_{11})/R = 573.78$ K $(\lambda_{12} - \lambda_{22})/R = 101.60$ K; Standard deviation in temperature, 0.3 K

T/°C	x_1	y_1	r_1	r_2	G^E/J mol^{-1}
Total pressure: 200 Torr					
48.2	0.0000	0.0000	7.0989	1.0000	0
46.3	0.0551	0.1118	4.9361	1.0102	259
45.8	0.1566	0.1887	3.0559	1.0679	608
46.0	0.2399	0.2188	2.3168	1.1430	805
46.1	0.3477	0.2463	1.7789	1.2745	952
46.5	0.4390	0.2679	1.5043	1.4199	999
47.2	0.5516	0.2992	1.2866	1.6532	971
47.9	0.6533	0.3387	1.1595	1.9321	868
49.9	0.7525	0.3992	1.0777	2.2902	703
52.9	0.8458	0.4995	1.0295	2.7338	488
59.9	0.9556	0.7676	1.0024	3.4350	158
64.3	1.0000	1.0000	1.0000	3.7826	0
Total pressure: 500 Torr					
73.9	0.0000	0.0000	6.541	1.0000	0
70.1	0.0551	0.1328	4.5016	1.0090	261
69.3	0.1567	0.2284	2.9109	1.0617	617
68.8	0.2399	0.2664	2.2452	1.1317	819
68.9	0.3477	0.3008	1.7448	1.2560	976
69.1	0.4390	0.3270	1.4845	1.3940	1024
70.0	0.5516	0.3634	1.2760	1.6156	997
71.0	0.6533	0.4074	1.1536	1.8798	898
72.2	0.7525	0.4717	1.0748	2.2175	722
75.5	0.8458	0.5721	1.0283	2.6331	501
81.8	0.9556	0.8134	1.0023	3.2852	162
85.9	1.0000	1.0000	1.0000	3.6090	0
Total pressure: 705 Torr					
84.7	0.0000	0.0000	5.8286	1.0000	0
80.5	0.0581	0.1401	4.3429	1.0085	261
79.1	0.1566	0.2428	2.8565	1.0592	621
78.7	0.2399	0.2840	2.2171	1.1274	825
78.8	0.3477	0.3210	1.7311	1.2488	982
79.1	0.4390	0.3489	1.4765	1.3849	1036
79.7	0.5516	0.3871	1.2717	1.6009	1008
80.6	0.6533	0.4325	1.1512	1.8594	903

Table 3 (*Continued*)

T/°C	x_1	y_1	r_1	r_2	G^E/J mol^{-1}
82.0	0.7525	0.4977	1.0735	2.1892	731
84.6	0.8458	0.5973	1.0278	2.5940	506
90.8	0.9556	0.8282	1.0023	3.2276	164
95.0	1.0000	1.0000	1.0000	3.5409	0

$$\ln \gamma_2 = -\ln [x_2 + \Lambda_{21} x_1] + x_1 \left[\frac{\Lambda_{21}}{x_2 + \Lambda_{21} x_1} - \frac{\Lambda_{12}}{x_1 + \Lambda_{12} x_2} \right] \tag{2}$$

where

$$\Lambda_{12} = \frac{v_2^L}{v_1^L} \exp - \left[\frac{\lambda_{12} - \lambda_{11}}{RT} \right] \tag{3}$$

$$\Lambda_{21} = \frac{v_1^L}{v_2^L} \exp - \left[\frac{\lambda_{21} - \lambda_{22}}{RT} \right] \tag{4}$$

where v_1^L and v_2^L are liquid molar volumes and $(\lambda_{12} - \lambda_{11})$ and $(\lambda_{12} - \lambda_{22})$ are the Wilson parameters; λ's are the energies of interaction between molecules designated by the subscripts. The optimum Wilson parameters $[(\lambda_{12} - \lambda_{11}/R]$ and $[(\lambda_{12} - \lambda_{22})/R]$ are obtained by minimizing the function ϕ, defined as

$$\phi = \Sigma\, [(P_{\text{cal}}/P_{\text{expt}}) - 1]^2 \tag{5}$$

The Nelder–Mead optimization technique described by Kuester and Mize [8] was used. Vapour pressures required in the computations were calculated from the Antoine constants given by Dean [9], and reproduced in Table 2 for ready reference. Liquid molar volumes were calculated from Yen and Woods [10] correlation. The values of the optimum Wilson parameters are also noted along with the detailed information on the observed bubble-point temperature (T) mole fraction of allyl alcohol in the liquid phase (x_1), and the calculated values of the mole fraction of allyl alcohol in the vapour phase (y_1), the liquid-phase activity coefficients (γ_1 and γ_2) and the excess Gibbs free energy (G^E) are presented in Table 3. The prospect of formation of azeotropic mixtures at different pressure as shown in Table 4, is predicted based on the model. Experimental investigation confirmed the formation of azeotropes, under the conditions noted in the

Table 4
Azeotropic conditions

Pressure/Torr	Temperature/°C	Mole fraction of propargyl alcohol
200	45.7	0.1980
500	68.8	0.2820
705	78.8	0.3210

table. The data and the representation presented in this paper are therefore expected to be reliable within the stated limits of experimental error.

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